



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 696 618 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
05.01.2000 Bulletin 2000/01

(51) Int Cl.7: **C08L 101/00, C08K 3/26,**
C08J 11/06
// (C08L101/00, 27:06)

(21) Application number: **95304744.6**

(22) Date of filing: **06.07.1995**

(54) **Thermoplastic resin compositions having improved performance**

Thermoplastische Harzzusammensetzungen mit verbesserter Leistung

Compositions de résin thermoplastique ayant une performance améliorée

(84) Designated Contracting States:
BE DE FR GB IT NL SE

(30) Priority: **13.07.1994 US 274592**

(43) Date of publication of application:
14.02.1996 Bulletin 1996/07

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(56) References cited:
EP-A- 0 260 820 WO-A-92/15640
WO-A-94/07950

- DATABASE WPI Derwent Publications Ltd.,
London, GB; AN 87-083930[12] & JP-A-62 035
806 (MITSUBISHI MOTOR CORP.) 16 February
1987
- DATABASE WPI Derwent Publications Ltd.,
London, GB; AN 84-156087[25] & JP-A-59 083
618 (MITSUBISHI BELTING KK) 15 May 1984

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Description**FIELD OF THE INVENTION:**

5 [0001] This invention pertains to compositions containing heat resistant polymers which have been contaminated with low levels of a vinyl chloride polymer such as polyvinyl chloride. More specifically, the invention relates to enhancing the performance of such contaminated compositions by incorporating calcium carbonate therein. Contaminated compositions reclaimed in this manner exhibit properties equivalent to those of the virgin (non-contaminated) thermoplastic resins and may be readily processed without causing accelerated machine and mold wear due to the generation of
10 acidic by-products.

BACKGROUND OF THE INVENTION:

15 [0002] In recent years, the recycling or reclamation of construction materials has become of increasing interest in view of the perceived need to conserve landfill space and non-renewable resources such as petroleum. By their nature, thermoplastic polymers are inherently recyclable in principle since they are materials with non-crosslinked macromolecular structures which will repeatedly soften when heated and reharden when cooled. Waste or scrap thermoplastic polymers thus may theoretically be reshaped into useful molded articles. In practice, however, great care must be taken to segregate waste streams by polymer type since the presence of even minor amounts of one polymer in another
20 may significantly degrade the physical and mechanical properties of the dominant polymer. Polymeric contaminants thus frequently prevent recycled polymers from being used interchangeably with virgin resins due to their adverse effect on quality.

[0003] An example of this is found in the reclamation of interior trim parts from automobiles and other vehicles which have been produced using a heat resistant polymer such as a styrene maleic anhydride copolymer or polyphenylene ether. It is common practice to place an outer skin on instrument panels and the like to enhance appearance. An intermediate layer such as a urethane foam may also be present to provide padding. The outer skin differs in composition from the underlying substrate and frequently contains a vinyl chloride polymer such as polyvinyl chloride compounded with plasticizers, colorants, and other additives. After the trimming operations common to instrument panel manufacture or after the instrument panel has been removed from the vehicle at the end of its useful service life, the
30 heat resistant polymer could in theory be formed into new trim parts by grinding or chopping into small particles and then remolding those particles by injection molding techniques. However, it is exceedingly difficult to remove essentially all of the outer skin from the trim part prior to such reuse through the use of solvent or mechanical separation means. The heat resistant polymer thus, for all practical purposes, is invariably contaminated with small amounts of polyvinyl chloride.

35 [0004] Such contamination makes direct recycling of the heat resistant polymer impractical. The heat resistant polymer must be processed and molded at relatively high temperatures. The vinyl chloride polymer contaminant is unstable at such elevated temperatures and tends to thermally degrade. This degradation adversely affects certain physical properties of the heat resistant thermoplastic polymer such as tensile strength/toughness and flex strength/toughness. Moreover, the acidic byproducts generated by the degradation of the vinyl chloride polymer accelerate machine and
40 mold wear.

[0005] As a result, there exists a need for methods whereby a heat resistant thermoplastic polymer contaminated with a vinyl chloride polymer such as polyvinyl chloride may be processed to provide a recycled resin composition at least equivalent in performance to non-contaminated polymer.

45 [0006] EP-A-0 260820 describes a stabilizer concentrate for use in stabilising polymer blends which include a thermally sensitive polymer. The concentrate comprises a blend of a carrier resin and a stabilizing agent capable of stabilizing the thermally sensitive polymer. The thermally sensitive polymers with which the publication is particularly concerned are vinylidene chloride interpolymers but polyvinyl chloride is also mentioned.

SUMMARY OF THE INVENTION:

50 [0007] The present invention provides a polymeric composition comprising 100 parts by weight of a thermoplastic resin comprised of a heat resistant polymer (preferably, one having a glass transition temperature greater than 100°C), from 0.01 to 5 parts by weight of a vinyl resin comprised of a vinyl chloride polymer, and from 0.01 to 5 parts by weight calcium carbonate. At least a portion of the thermoplastic resin is reclaimed. The invention additionally furnishes a
55 method of enhancing the performance of a reclaimed thermoplastic resin contaminated with from 0.01 to 5 parts by weight, per 100 parts by weight thermoplastic resin, of a vinyl resin comprised of a vinyl chloride polymer, wherein the thermoplastic resin is comprised of a heat resistant polymer, said method comprising incorporating at least 0.01 parts, and preferably from 0.01 to 5 parts, by weight calcium carbonate per 100 part by weight reclaimed thermoplastic resin

and at least 0.25 part by weight calcium carbonate per part by weight vinyl resin into said reclaimed thermoplastic resin.

[0008] The heat resistant polymer is selected from a (i) polyphenylene oxides, (ii) random styrenic copolymers comprised of, in polymerized form, 50 to 99 weight percent of a vinyl aromatic monomer, 1 to 30 weight percent of an unsaturated dicarboxylic acid derivative, and 0 to 40 weight percent of a copolymerizable ethylenically unsaturated monomer, (iii) aromatic polycarbonates, (iv) styrene-acrylonitrile copolymers, (v) acrylonitrile-butadiene-styrene polymers, and (vi) mixtures thereof.

[0009] Preferably, at least 5 parts by weight of the thermoplastic resin has been reclaimed.

[0010] In one desirable embodiment, the invention also provides a composition comprising 100 parts by weight of a reclaimed thermoplastic resin comprised of a styrene maleic anhydride copolymer, from 0.1 to 2 parts by weight at a vinyl resin comprised of polyvinyl chloride at least 0.1 parts by weight of finely divided calcium carbonate having an average particle size of from 0.07 to 100 microns, and, optionally, a virgin thermoplastic resin, wherein at least 0.5 part by weight calcium carbonate per part by weight vinyl resin is present.

DETAILED DESCRIPTION OF THE INVENTION:

[0011] This invention is useful for recycling or reclaiming vinyl chloride polymer contaminated thermoplastic resins from both preconsumer and postconsumer sources. Preconsumer sources include the scraps generated by a manufacturer in trimming a molded article or forming openings in such articles as well as complete molded articles which do not meet manufacturing specifications. Postconsumer sources include molded articles, e.g. interior automotive parts such as instrument panels, removed from automobiles, appliances, and the like which have reached the end of their useful service life.

[0012] The compositions provided by this invention contain a thermoplastic resin comprised of a heat resistant polymer selected from random styrenic copolymers, aromatic polycarbonates, SAN resins, ABS resins, polyphenylene oxides, and mixtures thereof. The thermoplastic resin component may contain other materials as well in addition to the heat resistant polymer, including, for example, any of the conventional plastic additives such as fillers (including glass fibers and the like), colorants, antioxidants, plasticizers, stabilizers and the like.

[0013] Suitable random styrenic copolymers include polymeric substances which, in polymerized form, are comprised of from about 50 to 99 weight percent of a vinyl aromatic monomer, from about 1 to 30 weight percent of an unsaturated dicarboxylic acid derivative, and, optionally, up to about 40 weight percent of a copolymerizable ethylenically unsaturated monomer. It is preferred that the random styrenic copolymer be comprised of from about 70 to 95 weight percent vinyl aromatic monomer and from about 5 to 30 weight percent unsaturated dicarboxylic acid anhydride.

[0014] Although any suitable vinyl aromatic monomer may be employed in the random styrenic copolymer, styrene is the preferred monomer because of its low cost and availability. Examples of other vinyl aromatic monomers which can be used include, but are not limited to, ar-methyl styrene, ar-ethyl styrene, ar-tert-butyl styrene, ar-chloro styrene, alpha-methyl styrene, divinyl benzene, vinyl benzyl chloride, and vinyl naphthalene, as well as other alkyl- or halo-substituted styrenes. Mixtures of vinyl aromatic monomers can be used.

[0015] The preferred unsaturated dicarboxylic acid derivative is an unsaturated dicarboxylic acid anhydride. Exemplary unsaturated dicarboxylic acid anhydrides include itaconic anhydride, citraconic anhydride, ethyl maleic anhydride, methyl itaconic anhydride, chloromaleic anhydride, brommaleic anhydride, tetrahydrophthalic anhydride, and, most preferably, maleic anhydride. However, other α,β -unsaturated dicarboxylic acid derivatives may also be employed including α,β -unsaturated dicarboxylic acids such as maleic or fumaric acid and maleimides such as N-methyl maleimide N-phenyl maleimide and N-tribromophenyl maleimide. If desired, mixtures of α,β -unsaturated dicarboxylic acid derivatives can be used.

[0016] The optional copolymerizable ethylenically unsaturated monomer may be selected from the group consisting of unsaturated nitriles (e.g., acrylonitrile and methacrylonitrile), unsaturated carboxylic acids (e.g., acrylic acid and methacrylic acid), unsaturated carboxylic acid esters (especially C_1 - C_4 alkyl esters such as methyl methacrylate and ethyl acrylate), and mixtures thereof. Terpolymers of styrene, maleic anhydride and acrylonitrile or styrene, maleic anhydride and methyl methacrylate are particularly preferred.

[0017] In the most preferred embodiment of this invention, the random styrenic copolymer is a copolymer of styrene and maleic anhydride. The random styrenic copolymer preferably has a number average molecular weight of from about 30,000 to 500,000 and a melt flow rate (Condition L) of from about 0.1 to 10 g/10 min.

[0018] Impact-modified random styrenic copolymers may also be employed. Such copolymers preferably contain from about 1 to 35 (more preferably, from about 5 to 25) weight percent of an elastomer. The elastomer is preferably selected from the group consisting of conjugated diene elastomers and ethylene-propylene-diene monomer elastomers.

[0019] Conjugated diene elastomers suitable for use as the elastomer preferably contain at least about 50 weight percent of a conjugated diene and have glass transition temperatures less than about 0°C (more preferably, less than about -20°C.). Such elastomers include homopolymers, random copolymers, and block copolymers of conjugated

1,3-dienes such as 1,3-butadiene (a preferred diene), isoprene, chloroprene, 1,3-pentadiene and 2,3-dimethyl-1,3-butadiene. The conjugated diene elastomer is preferably selected from the group consisting of mono-vinyl aromatic monomer/-conjugated diene block copolymers, mono-vinyl-aromatic monomer/conjugated diene random copolymers, conjugated diene homopolymers, and mixtures thereof.

5 [0020] The conjugated diene elastomer may contain one or more copolymerizable ethylenically unsaturated comonomers. Most preferably, the comonomer is a mono-vinyl aromatic monomer such as styrene, ar-methyl styrene, ar-ethyl styrene, ar-tert-butyl styrene, ar-chlorostyrene, alpha-methyl styrene, vinyl benzyl chloride or vinyl naphthalene and mixtures thereof. Other copolymerizable ethylenically unsaturated monomers may be employed, however, including unsaturated nitrile monomers such as acrylonitrile and methacrylonitrile, alkyl acrylates such as methyl methacrylate, methyl acrylate, butyl acrylate, or 2-ethyl-hexyl methacrylate, acrylamides such as acrylamide, methacrylamide, or butylacrylamide, unsaturated ketones such as vinyl methyl ketone or methyl isopropenyl ketone, α -olefins such as ethylene or propylene, vinyl esters such as vinyl acetate or vinyl stearate, vinyl heterocyclic monomers such as vinyl pyridine, and vinyl and vinylidene halides such as vinyl chloride or vinylidene chloride, and mixtures thereof. In a preferred embodiment of this invention, the comonomer used in combination with the 1,3-conjugated diene is the same as the vinyl aromatic monomer component of the random styrenic copolymer.

15 [0021] Exemplary conjugated diene elastomers suitable for grafting onto the random thermoplastic copolymer include styrene/butadiene and styrene/isoprene block copolymers. Such block copolymers may be linear, radical, or branched in structure. Linear block copolymers may have an ABA, AB(AB)_nA, (AB)_n, or similar structure wherein A represents a block of the monovinyl aromatic monomer, B represents a block of the conjugated diene and n is an integer of 1 to 10. Radical block copolymers may have an (AB)_nX structure, wherein X is a multi-valent linking agent. Block copolymers of these types are well-known. Details concerning their preparation, structure, and properties may be found, for example, in the following references: "Styrene-Diene Block Copolymers" *Encyclopedia of Polymer Science and Technology* 1st Ed., Suppl., Wiley, pp 508-530(1971), K. E. Snavely et al, *Rubber World* 169, 45(1973), and "Thermoplastic Elastomers" *Kirk-Othmer Encyclopedia of Chemical Technology* 3rd. Ed., Vol. 8, Wiley-Interscience, pp 627-632 (1981).

25 [0022] The following U.S. patents further describe such block copolymer conjugated diene elastomers: U.S. Pat. Nos. 3,937,760, 3,231,635, 3,265,765, 3,198,774, 3,078,254, 3,244,644, 3,280,084, 3,954,452, 3,766,301, 3,281,383, 4,640,968, 4,503,188, 4,485,210, 4,390,663, 4,271,661, and 4,346,193. Suitable block copolymers are also presently available from commercial sources. Examples of commercially available block copolymer elastomers include "Stereon 840A" (a linear graded styrene/butadiene multi-block copolymer containing about 43% styrene and having a number average molecular weight of about 60,000, sold by Firestone Synthetic Rubber and Latex Co.), "Stereon 730A" (a stereospecific tapered styrene/butadiene block copolymer containing a total of 30% styrene with 21% styrene in block form and having a number average molecular weight of 140,000, sold by Firestone Synthetic Rubber and Latex Company), "Kraton D-1101" (a linear styrene/butadiene/styrene triblock copolymer containing 31% styrene, sold by Shell Chemical), "Kraton D-1107" (a linear styrene/isoprene/styrene triblock copolymer containing 14% styrene, sold by Shell Chemical), "Kraton D-1107" (a linear styrene/isoprene/styrene triblock copolymer containing 14% styrene, sold by Shell Chemical), and "Kraton D-1184" (a branched styrene/butadiene multiblock copolymer containing 30% styrene, sold by Shell Chemical).

30 [0023] Also suitable for use as conjugated diene elastomers in the rubber-modified styrenic resin component of this invention are random copolymers of mono-vinyl aromatic monomers and conjugated dienes. A particularly preferred conjugated diene elastomer of this type is styrene/butadiene rubber (SBR). Homopolymers of conjugated dienes such as polybutadiene and polyisoprene may also be employed as the grafted rubber. All such rubbers are well-known in the art and are described, for example, in "Butadiene Polymers" *Encyclopedia of Polymer Science and Engineering* 2nd Ed., Wiley-Interscience, Vol. 2, pp. 537-590(1988).

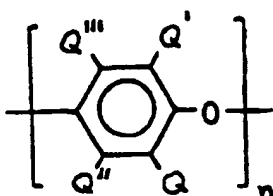
45 [0024] The grafted elastomer may alternatively be an ethylene propylene diene monomer (EPDM) rubber. Such materials are well-known in the art and are random copolymers of ethylene, at least one C₃-C₆ α -olefin (preferably propylene), and at least one nonconjugated diene. The nonconjugated diene may be a linear aliphatic diene of at least six carbon atoms which has either two terminal double bonds or one terminal double bond and one internal double bond. Alternatively, the nonconjugated diene may be a cyclic diene where one or both of the double bonds are part of a carbocyclic ring. The structure of the EPDM rubber may be altered as desired, particularly with respect to branching, by the selection of particular nonconjugated dienes as is well known in the art. Particularly preferred nonconjugated dienes include 1,4-hexadiene, dicyclopentadiene, vinyl norbornene, norbornadiene, and 5-ethylidene-2-norbornene. Preferably, the EPDM elastomer contains from about 40 to 90 mole percent ethylene and 0.1 to 7.5 mole percent nonconjugated diene, with the remainder being propylene. Additional information regarding EPDM elastomers may be found in "Ethylene-Propylene Elastomers" *Encyclopedia of Polymer Science and Engineering* 2nd Ed., Wiley-Interscience, Vol.6, p. 522-564(1986).

55 [0025] The random styrenic copolymers useful in the compositions of this invention may be prepared by any of the several methods available for their synthesis. For example, the copolymers may be obtained by solution copolymerization directly from the respective monomers by the incremental addition of the more reactive monomer as taught by

U.S. Pat. No. 2,971,939 or by a continuous recycle polymerization process described in U.S. Pat. Nos. 2,769,804 and 2,989,517. Alternatively, a suspension polymerization process as taught in U.S. Pat. No. 3,509,110 may be employed. Impact-modified random styrenic copolymers may be prepared by incorporation of the elastomer into the monomer mixture prior to polymerization using, for example, the methods of U.S. Pat. Nos. 4,097,551 and 3,919,354. Post-synthesis blending of all or part the elastomer into the random styrenic copolymer is also feasible. The teachings of all these patents are incorporated herein by reference. Suitable commercially available random styrenic copolymers include the "Dylark" styrene/maleic anhydride resins produced by ARCO Chemical Company, as well as the "Stapron" resins produced by DSM and the "Cadon" resins produced by Monsanto.

[0026] The term "polyphenylene oxide" (used interchangeably herein and in the art with the term "polyphenylene ether") is well known as defining a class of heat resistant polymers. See, for example, the article by Aycode et al. entitled "Poly (phenylene) Ether", which appears in the Encyclopedia of Polymer Science & Engineering, Vol. 13, pp. 1-30 (1988).

[0027] While any polyphenylene oxide resin may be employed in the compositions of the present invention, preferred are homo- and copolymeric resins having the formula:

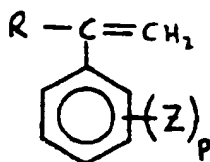


wherein the oxygen ether atom of one unit is connected to the benzene nucleus of the next adjoining unit, n represents the number of monomer units and is a positive integer of at least 50, e.g., from 50 to about 200, and Q, Q', Q'', and Q''' are independently selected from the group consisting of hydrogen, halogen, hydrocarbon radicals free of a tertiary alpha-carbon atom, halohydrocarbon radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus, hydrocarboxy radicals and halohydrocarboxy radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus.

[0028] Still more preferably, within the above formula Q and Q' are alkyl, especially alkyl having from 1 to 4 carbon atoms. Illustratively, such resins include poly(2,6-dimethyl-1,4-phenylene)ether; poly(2,6-diethyl-1,4-phenylene)ether; poly(2-methyl-6-ethyl-phenylene) ether; poly(2-methyl-6-propyl-1,4-phenylene)ether; poly(2,6-dipropyl-phenylene) ether and poly(2-ethyl-6-propyl 1,4-phenylene)ether.

[0029] Especially preferred is poly(2,6-dimethyl-1,4-phenylene)ether, preferably having an intrinsic viscosity of from about 0.4 to 0.8, more preferably about 0.45 deciliters per gram (dl/g.) measured in solution in chloroform at 30°C.

[0030] These polyphenylene oxides also may desirably contain styrene resin to improve their physical properties. Suitable styrene resins are those having at least 25% by weight of repeating units derived from a vinyl aromatic compound of the formula:



wherein R is hydrogen, (lower)alkyl or halogen; Z is vinyl, halogen or (lower)alkyl; and p is 0 or an integer from 1 to the number of replaceable hydrogen atoms on the benzene nucleus. Herein, the term "(lower)alkyl" means alkyl of from 1 to 6 carbon atoms.

[0031] The term "styrene resin" includes, by way of example, homopolymers such as polystyrene and polychlorostyrene, as well as polystyrenes which have been modified by natural or synthetic rubber (HIPS), e.g., polybutadiene, polyisoprene, butyl rubber, EPDM rubber, ethylene propylene copolymers, natural rubber, polysulfide rubbers, polyurethane rubbers and epichlorohydrin; styrene containing copolymers such as the styrene-acrylonitrile copolymers (SAN), styrene-butadiene copolymers, styrene-maleic anhydride copolymers, styrene-acrylonitrile-butadiene terpolymers (ABS), poly-alpha-methylstyrene and copolymers of ethylvinylbenzene and divinylbenzene; block copolymers of

the A-B-A and A-B type wherein A is polystyrene and B is an elastomeric diene, e.g., polybutadiene, radial teleblock copolymers of styrene and a conjugated diene, acrylic resin modified styrenebutadiene resins and blends of homopolystyrene and copolymers of the aforementioned types.

[0032] The styrene resin may be present in any amount. Widely divergent proportions of from 1:99 to 99:1 by weight of polyphenylene oxide resin are known. More desirably the respective styrene and polyphenylene ether resins are in a weight ratio of from about 2:1 to 1:20, most preferably about 1:4, for use in the present compositions.

[0033] Methods of preparing polyphenylene oxide resins are known in the art and described in the patent literature, e.g., Hay, U.S. Pat. Nos. 3,306,874, and 3,306,875 and Stamatoff, U.S. Pat. Nos. 3,257,358, incorporated by reference to save unnecessary detail. Other patents which show the preparation of polyphenylene oxide resins include Bennett and Cooper, U.S. Pat. Nos. 3,369,656 and 3,838,102, as well as Cooper and Bennett, U.S. Pat. Nos. 3,642,699, and 3,733,299.

[0034] Polyphenylene oxide resins also readily available from commercial sources, including General Electric ("Noryl" resins). "Noryl GTX" resins, which are alloys of poly(2,6-dimethyl-1,4-phenylene ether) and a polyamide such as nylon 6 or nylon 6,6, are also suitable for use as the polyphenylene oxide component.

[0035] Aromatic polycarbonates may also be used as the heat resistant polymer component. Such materials are well known in the field and are generally described, for example, in Freitag et al., "Polycarbonates," Encyclopedia of Polymer Science and Engineering, Vol. 11, pp. 650 - 718 (1988). Aromatic polycarbonates are typically prepared by the interfacial polymerization of bisphenols such as bisphenol A and either phosgene or diphenyl carbonate. Commercial suppliers of suitable aromatic polycarbonates include Dow Chemical ("Calibre" resins), GE Plastics ("Lexan" resins), Mobay Corp. ("Apec" resins), and Rohm & Haas ("Tuffak" resins). The aromatic polycarbonate may be blended with another polymeric substance such as polyethylene, ABS, polyalkylene terephthalate, or a styrene maleic anhydride copolymer.

[0036] Also useful as the heat resistant polymer is the class of resins commonly referred to as acrylonitrile-butadiene-styrene (ABS) polymers such as those described in Kulich et al., "Acrylonitrile-Butadiene-Styrene Polymers", Encyclopedia of Polymer Science and Engineering, Vol. 1, pp. 388-426 (1985). The high heat ABS grades are especially advantageous for use in the present invention. ABS polymers may be obtained commercially from Dow Chemical ("Magnum" resins), Monsanto ("Lustran ABS" resins) and GE Plastics ("Cyclocac" resins).

[0037] Styrene-acrylonitrile (SAN) resins may also be utilized as the heat resistant polymer. Such resins are typically copolymers of styrene and acrylonitrile or analogous monomers and are described, for example, in Peng, "Acrylonitrile Polymers", Encyclopedia of Polymer Science and Engineering, Vol. 1, pp. 452-464 (1988). Commercial grades of SAN polymers include "Tyrl" resins (Dow Chemical) and "Lustran SAN" resins (Monsanto).

[0038] The vinyl resin component is comprised of a vinyl chloride polymer such as polyvinyl chloride or chlorinated polyvinyl chloride. Vinyl chloride polymers and vinyl resins prepared therefrom are well known in the art and are described, for example, in "Vinyl Chloride Polymers", Encyclopedia Polymer Science & Engineering, Supplement pp. 858-884 (1989) and Davidson et al., "Vinyl Polymers (PVC)", Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Ed., Vol. 23, pp. 886-936 (1983). Such materials are formed by the polymerization of vinyl chloride monomer, either alone or with a comonomer such as other unsaturated halogenated hydrocarbons (e.g., vinylidene chloride), styrene and halogenated styrenes, vinyl esters and ethers (e.g., vinyl acetate, vinyl isobutyl ether), olefins (e.g., propylene), dienes, unsaturated nitriles (e.g., acrylonitrile), esters and other derivatives of acrylic and methacrylic acid (e.g., 2-ethyl hexyl acrylate), and olefinic dicarboxylic acids and esters. The vinyl chloride polymer may be impact modified with a modifier such as MBS, ABS, acrylic rubber, chlorinated polyethylene or EVA copolymer. In addition to the vinyl chloride polymer, the vinyl resin component may contain, for example, plasticizers, lubricants, antistatic agents, pigments, flame or fire retardants, stabilizers, high polymeric processing aids and other polymers. Typically, the vinyl resin will be comprised of from about 20 to 60 weight percent vinyl chloride polymer. Suitable vinyl resins are available from commercial sources such as B.F. Goodrich ("Geon" resins).

[0039] The calcium carbonate may be any of the various finely divided grades conventionally used as fillers or reinforcements for plastics and preferably has a particle size of from 0.07 to 100 microns. Natural or synthetic calcium carbonate may be utilized, including purified ground CaCO_3 , dry processed CaCO_3 and precipitated CaCO_3 . It is critical to incorporate a sufficient amount of CaCO_3 into the thermoplastic resin and vinyl resin so as to prevent any significant loss in physical or mechanical properties when the latter two components are melt processed at elevated temperature. While from 0.01 to 5 parts by weight CaCO_3 per 100 parts by weight thermoplastic resin may be utilized, in general it will be highly advantageous to have a calcium carbonate level at least roughly equal to the concentration of the vinyl resin present. Preferably, at least 0.25 parts by weight (more preferably, at least 0.5 parts by weight) calcium carbonate per part by weight vinyl resin is present. In one embodiment, the weight ratio of calcium carbonate to vinyl resin is in the range 1:4 to 4:1.

[0040] In one embodiment, the present invention is useful in reclaiming a vinyl resin skin clad thermoplastic polymer comprising a vinyl resin skin and a substrate of molded thermoplastic resin comprised of the heat resistant polymer. The skin may be adhered directly to the substrate, or, alternatively, to a layer of polyurethane foam or the like (which provides padding) which in turn is attached to the substrate. A barrier film and/or adhesive may also be present

between the polyurethane foam layer and the substrate. The vinyl resin skin performs at least two functions. The first is to provide a suitable "show surface", where the clad thermoplastic polymer is to be visible when in use. For example, the clad thermoplastic polymer may be formed into an instrument panel for automotive application. The outer texture and color of the instrument panel should match the other similar surfaces of the automobile interior. By using a vinyl resin comprised of a vinyl chloride polymer to cover the outer surface of the underlying substrate containing a layer of thermoplastic resin and (optionally) other layers such as a polyurethane foam layer, the desirable properties of the thermoplastic resin layer such as rigidity can be retained while the vinyl resin is colored and textured to match other trim parts such as door panel moldings. The vinyl resin skin can also be employed to protect the substrate from damaging environmental conditions such as moisture and ultraviolet radiation. An adhesive may be utilized to bond the vinyl resin skin, thermoplastic resin substrate, and polyurethane foam layers to each other, while in certain instances the layers may be attached directly. This invention also has the advantage of substantially improving the performance of a recycle containing such an adhesive, which, if solvent-based, otherwise tends to embrittle the thermoplastic resin. The vinyl resin skin will typically be a thin film having a thickness of from about 0.05mm to about 0.5mm, whereas the thermoplastic resin substrate generally will be substantially thicker (typically, 1 to 5 mm).

[0041] To reclaim the vinyl resin skin clad thermoplastic polymer, the molded article comprised of the composite is preferably first physically removed or separated from other articles of dissimilar composition which may be present. For example, where the molded article is an automobile instrument panel installed in a finished vehicle, the bolts, screws, or other fasteners holding the panel in place are unfastened and the panel taken out of the automobile to be scrapped. Other components such as gauges and the like should be removed from the instrument panel. The molded article separated in this manner then is converted into particulate form to facilitate separation and recycling back into a molded article in combination with calcium carbonate and, generally, virgin thermoplastic resin. A variety of size reduction means are well known in the art and any such suitable means may be employed in this invention. For example, the molded article can be subjected to a shredding, chopping, crushing, grinding, or pulverization operation. If desired, the molded article may first be treated so as to remove a portion of the vinyl resin skin by mechanical or other such means, but one important advantage of this invention is that such further pretreatment is not necessary in order to reclaim the thermoplastic resin. The average diameter of the particles obtained from the molded article should preferably be less than about 2cm, but more preferably is from about 5 to 15 mm. The particles will typically contain about 0.01 to 5 parts by weight of vinyl resin per 100 parts by weight of the thermoplastic resin.

[0042] In one embodiment, which is particularly desirable where the molded article contains a polyurethane foam layer intermediate to the vinyl resin skin and the thermoplastic resin layer, the particles are subjected to a separation process in order to obtain a more highly pure recycle. Suitable separation processes for this purpose include solvent and mechanical based processes. Air classification and hydrocyclones typify the mechanical separation processes. Solvent separation processes include the process described in German Pat. Application P 4033604.2 (laid open April 30, 1992). If a solvent separation process is utilized, a solution of the thermoplastic resin (contaminated with the vinyl resin containing the vinyl chloride polymer) is typically obtained. The thermoplastic resin may be recovered in solid particulate form by removing the solvent by a suitable means such as evaporation or distillation or by a precipitation technique. Such recovered particles may thereafter be compounded with the calcium carbonate.

[0043] Calcium carbonate is physically combined with the particles containing the vinyl resin and the thermoplastic resin using an appropriate mixing technique prior to or coincidental with re-melting of the particles. It is critical that the calcium carbonate and the particles be simultaneously present when heating the solid particles so as to form a processable liquified mixture in order to maintain optimum properties in the resulting reclaimed thermoplastic resin.

[0044] The particles and the calcium carbonate (either in as-supplied form or in a suitable concentrate also containing thermoplastic resin) may be dry mixed at room temperature or slightly higher temperatures using, for example, dry tumbling of the two components or grinding or milling the particles for more thorough mixing. It will generally be desirable to employ a method which ultimately results in a uniform mixture wherein the calcium carbonate (usually in the form of a fine powder) is brought into intimate contact with the particles. For example, the calcium carbonate may form a thin coating on the surface of the particles. Any suitable type of mixing equipment may be employed such as an intensive internal mixer (e.g., Banbury high shear mixer, Farrel continuous mixer, Plastimat plasticator, turbulent mixer, or roll mill), a dry mixer or blender (e.g., ribbon blender, cone blender, vortical intensive mixer, ball mill, or double planetary mixer), or a rotary tumbler (e.g., drum tumbler, or conical dry blender). The calcium carbonate and particles may be simultaneously mixed and extruded using an extruder such as a single screw extruder, twin screw extruder, or mixer extruder. The product exiting from the extruder may be pelletized or otherwise converted into a form which may be readily handled and further processed. A mixture of calcium carbonate and particles obtained by dry mixing may be similarly extruded and pelletized. The pellets thereby produced then can be formed into molded articles using any of the procedures useful for molding virgin thermoplastic resin (e.g., injection molding, thermoforming, blow molding, extrusion, or foam molding). Direct molding of the particles together with the calcium carbonate may also be practised. The reclaimed pellets may, if so desired, be blended or combined with pellets of virgin resin prior to such reuse. Typically, the weight ratio of vinyl resin-contaminated (reclaimed) thermoplastic resin to virgin resin in such application will range

from 0.1:99.1 to 20:80. In another embodiment, the calcium carbonate may be first combined with virgin thermoplastic resin and the resulting product thereafter blended with the vinyl chloride polymer-contaminated thermoplastic resin particles. Dry tumbling methods will be useful for such purpose.

EXAMPLES

[0045] The following examples demonstrate the utility of the invention in improving the properties of a thermoplastic resin contaminated with a polyvinyl chloride-containing resin. In each example, the heat resistant polymer used was Dylark 378P20A, a glass fiber-reinforced styrene maleic anhydride copolymer resin containing minor amounts of acrylic regrind produced by ARCO Chemical Company. The formulations were processed using a single screw extruder at a melt temperature of about 260°C. Comparative Example 1 was prepared using virgin Dylark 378P20A resin only, which was molded as is into ASTM test bar specimens. Comparative Example 2 contained 0.5 weight percent of a vinyl resin in addition to the thermoplastic resin. The vinyl resin containing polyvinyl chloride was introduced in the form of a vinyl skin cut into small pieces using a paper cutter. The vinyl skin pieces were dry blended by hand with the Dylark resin and the resulting blend injection molded into ASTM test bar specimens at a melt temperature of about 250°C. Significant deterioration in tensile strength, elongation, tensile toughness, flex strength, and flex toughness were observed (Table 1). Each of these properties was restored to approximately the same level as in Comparative Example 1 by the addition of 0.8 weight % calcium carbonate, as illustrated in Example 3. The Dylark resin was first compounded with the CaCO₃ using a single screw extruder at melt temperature of about 260°C, then combined with the vinyl resin as described for Example 2.

TABLE 1

Example No.	1	2	3
Vinyl Resin, Wt %	0	0.5	0.5
CaCO ₃ , Wt %	0	0	0.8
Tensile Strength @ Break (psi)	11170 ± 151	10350 ± 266	10940 ± 104
Young's Modulus (ksi)	942 ± 144	1071 ± 197	982 ± 168
Elongation @ Break (%)	2.196 ± .07	1.927 ± .17	2.218 ± .19
Tensile Toughness (psi)	159 ± 7	130 ± 14	158 ± 7
Flex Strength @ Break (psi)	17510 ± 347	16340 ± 665	17720 ± 124
Flex Modulus (psi)	881 ± 20	908 ± 8.6	923 ± 5.4
Flex Toughness (psi)	24.7 ± 2	20.2 ± 2	24.3 ± .9
psi means pounds force per square inch. 1 psi = 6.895 kPa			
Ksi means kilopounds force per square inch. 1 Ksi = 6.895 MPa			

[0046] The following example demonstrates that the performance of a post-consumer recycle obtained by reclamation of styrene maleic anhydride copolymer resin-based instrument panels contaminated with both a vinyl chloride polymer and a solvent-based adhesive may be significantly enhanced using the present invention. The recycle was obtained from 1982-84 model year automobiles and contained 0.13 weight percent vinyl resin as an impurity. As compared to virgin styrene maleic anhydride copolymer resin of equivalent composition (other than the vinyl resin and adhesive contaminant), the recycle exhibited inferior properties:

PROPERTY	% RETENTION
Tensile Strength	81
Tensile Elongation	74
Flexural Strength	86
Flexural Modulus	99

[0047] Even when combined at only a 10% level with virgin styrene maleic anhydride copolymer resin, the recycle had an adverse impact on the quality of the resin blend (Example 4). The addition of 1 weight percent calcium carbonate, however, restored the resin blend performance to nearly that of the virgin uncontaminated resin (Example 5):

COMPOSITION	% BY WEIGHT	
	EXAMPLE 4	EXAMPLE 5
Virgin Resin	90	89
Recyclate	10	10
Calcium Carbonate	0	1

PROPERTY	% RETENTION	
	EXAMPLE 4	EXAMPLE 5
Tensile Strength	82	100
Tensile Elongation	90	100
Flexural Strength	93	98

Claims

1. A composition comprising:

(a) 100 parts by weight of a thermoplastic resin comprised of a heat resistant polymer selected from (i) polyphenylene oxides, (ii) random styrenic copolymers comprised of, in polymerized form, 50 to 99 weight percent of a vinyl aromatic monomer, 1 to 30 weight percent of an unsaturated dicarboxylic acid derivative, and 0 to 40 weight percent of a copolymerizable ethylenically unsaturated monomer, (iii) aromatic polycarbonates, (iv) styrene-acrylonitrile copolymers, (v) acrylonitrile-butadiene-styrene polymers, and (vi) mixtures thereof, wherein at least a portion of said thermoplastic resin has been reclaimed;

(b) from 0.01 to 5 parts by weight of a vinyl resin comprised of a vinyl chloride polymer; and

(c) from 0.01 to 5 parts by weight calcium carbonate.

2. A composition as claimed in claim 1 characterised in that the heat resistant polymer is a random styrenic copolymer comprised of, in polymerized form, 3 to 25 weight percent maleic anhydride and 75 to 97 weight percent styrene.

3. A composition as claimed in claim 2 characterised in that the random styrenic copolymer is impact modified.

4. A composition as claimed in claim 1 characterised in that the thermoplastic resin is comprised of polyphenylene oxide and polystyrene.

5. A composition as claimed in any preceding claim characterised in that the vinyl chloride polymer is polyvinyl chloride.

6. A composition as claimed in any preceding claim characterised in that at least 0.25 part by weight calcium carbonate per part by weight vinyl resin is present.

7. A composition as claimed in any preceding claim characterised in that the calcium carbonate is in the form of fine particles having an average particle size of from 0.07 to 100 μm (microns).

8. A composition as claimed in any preceding claim characterised in that at least 5 parts by weight of the thermoplastic resin has been reclaimed.

9. A composition as claimed in claim 1 or claim 2 comprising

(a) 100 parts by weight of a reclaimed thermoplastic resin comprised of a styrene maleic anhydride copolymer;

(b) from 0.1 to 2 parts by weight of a vinyl resin comprised of polyvinyl chloride; and

(c) at least 0.1 parts by weight of finely divided calcium carbonate having an average particle size of from 0.07 to 100 μm (microns);

wherein at least 0.5 part by weight calcium carbonate per part by weight vinyl resin is present.

10. A composition as claimed in claim 9 additionally comprising a virgin thermoplastic resin which may be the same as or different from the reclaimed thermoplastic resin in (a).

11. A composition as claimed in claim 9 or claim 10 characterised in that no more than 5 parts by weight calcium carbonate is present per 100 parts by weight total of reclaimed thermoplastic resin and virgin thermoplastic resin.

12. A method of enhancing the performance of a reclaimed thermoplastic resin contaminated with from 0.01 to 5 parts by weight, per 100 parts by weight thermoplastic resin, of a vinyl resin comprised of a vinyl chloride polymer, wherein the thermoplastic resin is comprised of a heat resistant polymer selected from (i) polyphenylene oxides, (ii) random styrenic copolymers comprised of, in polymerized form, 50 to 99 weight percent of a vinyl aromatic monomer, 1 to 30 weight percent of an unsaturated dicarboxylic acid derivative, and 0 to 40 weight percent of a copolymerizable ethylenically unsaturated monomer, (iii) aromatic polycarbonates, (iv) styrene-acrylonitrile copolymers, (v) acrylonitrile-butadiene-styrene polymers, and (vi) mixtures thereof; said method comprising incorporating at least 0.01 parts by weight calcium carbonate per 100 parts by weight of the reclaimed thermoplastic resin and at least 0.25 part by weight calcium carbonate per part by weight vinyl resin into said reclaimed thermoplastic resin.

13. A method as claimed in claim 12 characterised in that the reclaimed thermoplastic resin contaminated with the vinyl resin is obtained by recycling an interior automotive part.

14. A method as claimed in claim 13 characterised in that the interior automotive part is an instrument panel.

15. A method as claimed in claim 13 or claim 14 characterised in that the interior automotive part has a composite structure comprised of (a) a substrate comprised of the thermoplastic resin and (b) a skin comprised of the vinyl resin.

16. A method as claimed in any one of claims 13 to 15 characterised in that the interior automotive part is comminuted to form a plurality of particles prior to incorporation of the calcium carbonate.

17. A method as claimed in claim 15 characterised in that the composite structure is additionally comprised of (c) a polyurethane foam layer intermediate the substrate and the skin.

18. A method as claimed in claim 16 or claim 17 characterised in that the particles are dry mixed with the calcium carbonate.

19. A method as claimed in claim 16 or claim 17 characterised in that the particles and the calcium carbonate are co-extruded and pelletized.

20. A method as claimed in any one of claims 12 to 19 characterised in that the weight ratio of calcium carbonate to vinyl resin is from 4:1 to 1:4.

21. An article molded from a polymer material comprising a composition as claimed in any one of claims 1 to 11 or obtained by the method claimed in any one of claims 12 to 20.

Patentansprüche

1. Zusammensetzung, umfassend

(a) 100 Gewichtsteile eines thermoplastischen Harzes, umfassend ein wärmebeständiges Polymer, das ausgewählt wird aus (i) Polyphenylenoxiden, (ii) statistischen Styrolcopolymeren, die 50 bis 99 Gew.-% eines vinylaromatischen Monomeren, 1 bis 30 Gew.-% eines ungesättigten Dicarbonsäurederivats und 0 bis 40 % eines copolymerisierbaren ethylenisch ungesättigten Monomeren in polymerisierter Form umfassen, (iii) aromatischen Polycarbonaten, (iv) Styrol-Acrylnitril-Copolymeren (v) Acrylnitril-Butadien-Styrol-Polymeren und (vi) deren Mischungen, wobei mindestens ein Teil des thermoplastischen Harzes zurückgewonnen wurde,

(b) 0,01 bis 5 Gewichtsteile eines Vinylchloridpolymer umfassenden Vinylharzes und

(c) 0,01 bis 5 Gewichtsteile Calciumcarbonat.

- 5 2. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das wärmebeständige Polymer ein statistisches Styrolcopolymer ist, das 3 bis 25 Gew.-% Maleinsäureanhydrid und 75 bis 97 Gew.-% Styrol in polymerisierter Form umfaßt.
- 10 3. Zusammensetzung nach Anspruch 2, dadurch gekennzeichnet, daß das statistische Styrolcopolymer in seiner Schlagzähigkeit modifiziert ist.
4. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das thermoplastische Harz Polyphenylenoxid und Polystyrol umfaßt.
- 15 5. Zusammensetzung nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß das Vinylchloridpolymer Polyvinylchlorid ist.
6. Zusammensetzung nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß mindestens 0,25 Gewichtsteil Calciumcarbonat pro Gewichtsteil Vinylharz vorliegt.
- 20 7. Zusammensetzung nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß das Calciumcarbonat in Form feiner Teilchen mit einer durchschnittlichen Teilchengröße von 0,07 bis 100 µm (microns) vorliegt.
8. Zusammensetzung nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß mindestens 5 Gewichtsteile des thermoplastischen Harzes zurückgewonnen wurden.
- 25 9. Zusammensetzung nach Anspruch 1 oder 2, umfassend
 - 30 (a) 100 Gewichtsteile eines zurückgewonnenen thermoplastischen Harzes aus einem Styrolmaleinsäureanhydrid-Copolymer;
 - (b) 0,1 bis 2 Gewichtsteile eines Vinylharzes aus Polyvinylchlorid und
 - (c) mindestens 0,1 Gewichtsteil eines fein zerteilten Calciumcarbonats mit einer durchschnittlichen Teilchengröße von 0,07 bis 100 µm (microns)
- 35 wobei mindestens 0,5 Gewichtsteil Calciumcarbonat pro Gewichtsteil Vinylharz vorliegt.
- 40 10. Zusammensetzung nach Anspruch 9, die zusätzlich ein frisches thermoplastisches Harz umfaßt, das das gleiche wie das zurückgewonnene thermoplastische Harz in (a) oder ein anderes sein kann.
11. Zusammensetzung nach Anspruch 9 oder 10, dadurch gekennzeichnet, daß nicht mehr als 5 Gewichtsteile Calciumcarbonat pro 100 Gewichtsteile des gesamten zurückgewonnenen thermoplastischen Harzes und des frischen thermoplastischen Harzes vorliegen.
- 45 12. Verfahren zur Verbesserung der Leistung eines zurückgewonnenen thermoplastischen Harzes, das auf 100 Gewichtsteile thermoplastisches Harz mit 0,01 bis 5 Gewichtsteilen eines ein Vinylchloridpolymer umfassenden Vinylharzes verunreinigt ist, wobei das thermoplastische Harz ein wärmebeständiges Polymer umfaßt, das aus (i) Polyphenylenoxiden, (ii) statistischen Styrolcopolymeren, die 50 bis 99 Gew.-% eines vinylaromatischen Monomeren, 1 bis 30 Gew.-% eines ungesättigten Dicarbonsäurederivats und 0 bis 40 Gew.-% eines copolymerisierbaren ethylenisch ungesättigten Monomeren umfassen, (iii) aromatischen Polycarbonaten, (iv) Styrol-Acrylnitril-Copolymeren (v) Acrylnitril-Butadien-Styrol-Polymeren und (vi) deren Mischungen ausgewählt wird, wobei bei dem Verfahren mindestens 0,01 Gewichtsteile Calciumcarbonat auf 100 Gewichtsteile des zurückgewonnenen thermoplastischen Harzes und mindestens 0,25 Gewichtsteil Calciumcarbonat pro Gewichtsteil Vinylharz in das wiedergewonnene thermoplastische Harz inkorporiert werden.
- 50 55 13. Verfahren nach Anspruch 12, dadurch gekennzeichnet, daß das zurückgewonnene, mit dem Vinylharz verunreinigte thermoplastische Harz durch Recycling eines Innenteils eines Automobils gewonnen wird.

14. Verfahren nach Anspruch 13, dadurch gekennzeichnet, daß es sich bei dem Innenteil des Automobils um ein Armaturenbrett handelt.
- 5 15. Verfahren nach Anspruch 13 oder 14, dadurch gekennzeichnet, daß der Innenteil des Automobils eine Verbundstruktur aufweist, die (a) ein aus dem thermoplastischen Harz bestehendes Substrat und (b) eine das Vinylharz umfassende Haut umfassen.
- 10 16. Verfahren nach einem der Ansprüche 13 bis 15, dadurch gekennzeichnet, daß der Innenteil des Automobils zerkleinert wird, um vor der Inkorporierung des Calciumcarbonats eine Vielzahl von Teilchen zu bilden.
17. Verfahren nach Anspruch 15, dadurch gekennzeichnet, daß die Verbundstruktur außerdem (c) eine Polyurethanschaumschicht umfaßt, die zwischen dem Substrat und der Haut liegt.
- 15 18. Verfahren nach Anspruch 16 oder 17, dadurch gekennzeichnet, daß die Teilchen trocken mit dem Calciumcarbonat vermischt werden.
19. Verfahren nach Anspruch 16 oder 17, dadurch gekennzeichnet, daß die Teilchen und das Calciumcarbonat koextrudiert und pelletisiert werden.
- 20 20. Verfahren nach einem der Ansprüche 12 bis 19, dadurch gekennzeichnet, daß das Gewichtsverhältnis von Calciumcarbonat zu Vinylharz 4 : 1 bis 1 : 4 beträgt.
- 25 21. Formgegenstand aus einem Polymermaterial, das eine Zusammensetzung nach einem der Ansprüche 1 bis 11 umfaßt bzw. nach dem Verfahren nach einem der Ansprüche 12 bis 20 hergestellt wurde.

Revendications

- 30 1. Composition comprenant :
 - 35 (a) 100 parties en poids d'une résine thermoplastique constituée d'un polymère résistant à la chaleur choisi à partir de (i) oxydes de polyphénylène, (ii) de copolymères styréniques aléatoires constitués de, sous forme polymérisée 50 à 99 % en poids d'un monomère aromatique de vinyle, 1 à 30%, en poids d'un dérivé de l'acide dicarboxylique insaturé, et 0 à 40% en poids d'un monomère insaturé éthyléniquement copolymérisable (iii) de polycarbonates aromatiques, (iv) de copolymères de styrène acrylonitrile, (v) de polymères acrylonitrile butadiène-styrène, et (vi) leurs mélanges, dans laquelle au moins une portion de la résine thermoplastique a été récupérée.
 - (b) de 0,01 à 5 parties en poids d'une résine de vinyle constituées d'un polymère de chlorure de vinyle ; et
 - 40 (c) de 0,01 à 5 parties en poids de carbonate de calcium.
2. Composition selon la revendication 1, caractérisée en ce que le polymère résistant à la chaleur est un copolymère styrénique aléatoire constitué, sous la forme polymérisée, de 3 à 25%, en poids d'anhydride maléique et 75 à 97%, en poids de styrène.
- 45 3. Composition selon la revendication 2, caractérisée en ce que le copolymère styrénique aléatoire est modifié par impact.
4. Composition selon la revendication 1, caractérisée en ce que la résine thermoplastique est constituée d'oxyde de polyphénylène et de polystyrène.
- 50 5. Composition selon l'une quelconque des revendications précédentes, dans laquelle le polymère de chlorure de vinyle est le chlorure de polyvinyle.
6. Composition selon l'une quelconque des revendications précédentes, caractérisée en ce que l'on a au moins 0,25 parties en poids de carbonate de calcium par parties en poids de résine de vinyle.
- 55 7. Composition selon l'une quelconque des revendications précédentes, caractérisée en ce que le carbonate de calcium se présente sous la forme de particules fines ayant une taille particulière moyenne de 0,07 à 100 microns.

8. Composition selon l'une quelconque des revendications précédentes, caractérisée en ce qu'il a été récupéré au moins 5 parties en poids de la résine thermoplastique.

9. Composition selon la revendication 1 ou 2, comprenant :

- (a) 100 parties en poids d'une résine thermoplastique récupérée constituée d'un copolymère d'anhydride maléique de styrène ;
- (b) de 0,1 à 2 parties en poids d'une résine vinylique composée de chlorure de polyvinyle ; et
- (c) au moins 0,1 partie en poids de carbonate de calcium finement divisé ayant une taille particulière moyenne de 0,07 à 100 microns,

dans laquelle on a au moins 0,5 parties en poids de carbonate de calcium par parties en poids de résine vinylique.

10. Composition selon la revendication 9, comprenant de plus une résine thermoplastique vierge qui peut être la même que ou différente de la résine thermoplastique récupérée dans (a).

11. Composition selon la revendication 9 ou la revendication 10, caractérisée en ce que l'on a pas plus de 5 parties en poids de carbonate de calcium pour 100 parties en poids au total de résine thermoplastique récupérée et de résine thermoplastique vierge.

12. Procédé pour activer la performance de la résine thermoplastique récupérée qui a été contaminée avec 0,01 à 5 parties en poids, pour 100 parties en poids de résine thermoplastique, d'une résine vinylique constituée d'un polymère de chlorure de vinyle, dans lequel la résine thermoplastique est constituée d'un polymère résistant à la chaleur choisi à partir de (i) oxydes de polyphénylène, (ii) copolymères styréniques aléatoires constitués de, sous la forme polymérisée, 50 à 99 % en poids d'un monomère aromatique de vinyle, 1 à 30% en poids d'un dérivé de l'acide dicarboxylique insaturé, et 0 à 40% en poids d'un monomère insaturé éthyléniquement copolymérisable (iii) polycarbonates aromatiques, (iv) copolymères styrène-acrylonitrile, (v) polymères acrylonitrile-butadiène styrène et (vi) leurs mélanges ; ce procédé comprenant l'incorporation d'au moins 0,01 partie en poids de carbonate de calcium pour 100 parties en poids de la résine thermoplastique récupérée et au moins 0,25 parties en poids de carbonate de calcium par partie en poids de résine de vinyle dans la résine thermoplastique récupérée.

13. Procédé selon la revendication 12, caractérisé en ce que la résine thermoplastique récupérée contaminée avec la résine vinylique est obtenue par recyclage d'une pièce automobile intérieure.

14. Procédé selon la revendication 13, caractérisé en ce que la pièce automobile intérieure est un tableau de commande.

15. Procédé selon la revendication 13 et la revendication 14, caractérisé en ce que la pièce automobile intérieure présente une structurée composite constituée de (a) un substrat comprenant la résine thermoplastique et (b) une pellicule constituée de résine vinylique.

16. Procédé selon l'une quelconque des revendications 13 à 15, caractérisé en ce que la pièce automobile interne est finement broyée en poudre pour former une pluralité de particules avant l'incorporation du carbonate de calcium.

17. Procédé selon la revendication 15, caractérisé en ce que la structure composite comprend de plus (c) une couche de mousse de polyuréthane intercalée entre le substrat et la pellicule.

18. Procédé selon la revendication 16 ou 17, caractérisé en ce que les particules sont mélangées à sec avec le carbonate de calcium.

19. Procédé selon la revendication 16 ou 17, caractérisé en ce que les particules et le carbonate de calcium sont co-extrudés et agglomérés.

20. Procédé selon l'une quelconque des revendications 12 à 19, caractérisé en ce que le rapport pondéral entre le carbonate de calcium et la résine vinylique est de 4 : 1 à 1 : 4.

21. Article moulé à partir d'un matériau polymère comprenant une composition selon l'une quelconque des revendications

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cations 1 à 11 ou obtenu par le procédé revendiqué dans l'une quelconque des revendications 12 à 20.

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